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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Bleaching of Kraft Pulp with Hydrosulfite

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ABSTRACT

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A method of strengthening oxidatively bleached kraft pulps (including recycled pulps) is taught wherein the pulp
5 is treated with hydrosulfite, formamidine sulfinic acid or a selected sulfoxylate at specified pH, temperature and retention times. Further strengthening is obtained by the addition of a selected quaternary ammonium compound or alkoxylated amine.

BLEACHING OF KRAFT PULP WITH HYDROSULFITE

Background of the Invention

5

This invention concerns a method for increasing the physical strength of oxidatively bleached kraft pulp including pulp being recycled.

There are several ways in which wood composed of
10 lignin, cellulose, hemicellulose and extractives is processed into pulp for the purpose of making paper. These methods include mechanical techniques and chemical techniques. The kraft pulping process, also known as the sulfate pulping process, is one of the two alkaline
15 chemical pulping processes used for pulp. The kraft process utilizes sodium hydroxide and sodium sulfide to chemically remove a majority of the lignin from the cellulose and hemicellulose. As a consequence, however, some of the cellulose and hemicellulose are also removed by
20 this process of lignin removal. A typical kraft cook removes 80% of the lignin, 50% of the hemicellulose, 10% of the cellulose and 90% of the wood extractives (fats and resins). Delignification in kraft pulping is driven by the concentration of the hydroxyl anion (OH^-). The sodium
25 sulfide reacts with water to produce sodium hydroxide and

sodium bisulfite. The presence of the bisulfite suppresses condensation reaction of quinone methides and enhances the cleavage of the phenolic ether bonds.

A major concern for all processes involved in
5 converting wood to pulp, especially in kraft techniques, is the effect of the pulping process on the physical strength of the pulp, especially the cellulose component. The physical strength of paper is related to the strength of the pulp from which the paper is made and to the degree of
10 interfiber hydrogen bonding present in the finished paper. Of the three major pulp components (lignin, hemicellulose and cellulose), the cellulose fibers are the most critical to pulp strength.

In the area of kraft pulps strength is of particular
15 importance because kraft pulps are used in applications such as packaging materials and bags where strength is an important consideration. The severe conditions of papermaking and printing make it advisable to keep or increase the pulp strength as much as possible so that the
20 end products are of good quality.

With respect to processing kraft pulp, one of the steps is bleaching. Oxidative bleaching stages such as chlorine, chlorine dioxide, sodium hypochlorite, hydrogen peroxide, oxygen and ozone must be carefully controlled to
25 minimize the effect of bleaching chemicals on the cellulose component of the pulp. Most of these bleaching agents cause at least some deterioration of pulp strength. In

addition, chlorine and chlorine dioxide are not favored environmentally. The use of ozone may cause more deterioration in pulp strength than chlorine compounds.

There have been some attempts to find environmentally acceptable alternatives to chlorine and chlorine dioxide for bleaching kraft pulp. R. P. Bradley, "Pulp Bleaching Agents and Technologies Substituting for Chlorine at North American Pulp Mills", Chemical Industries Newsletter, September-October 1991, pages 1, and 3-5, discusses work with oxygen, nitrogen dioxide, ozone, and sodium hydrosulfite as well as other chlorine containing compounds. N. Liebergott et al, "Lowering AOX Levels in the Bleach Plant", TAPPI Proceedings - 1991 Pulping Conference, pages 123-133, lists oxygen, peroxide, ozone, peracetic acid, hydrosulfite, chelating agents and thiourea dioxide as alternatives to bleaching with chlorine-containing compounds. N. Liebergott et al, "Bleaching a Softwood Kraft Pulp Without Chlorine Compounds", TAPPI Journal - August 1984, pages 76-80, discusses bleaching using sequential stages including the use of sodium hydrosulfite as the final bleaching stage of a fully delignified chemical kraft pulp. None of these references, however, discusses a method for bleaching kraft pulp while increasing strength.

Thus, it is an object of this invention to provide a method of treating oxidatively bleached kraft pulp including wood pulp and pulp from recycled sources with a

member selected from the group consisting of hydrosulfite, formamidine sulfinic acid (FAS), and a sulfoxylate (such as sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate and acetaldehyde sulfoxylate), which method
5 increases the strength of the pulp while still maintaining or improving brightness. It is a further object of this invention to provide a method for bleaching kraft pulp which reduces the need for using chlorine containing compounds in the bleaching process. These and other
10 objects of this invention will be apparent from the description of the invention.

Summary of the Invention

15 The method of this invention may be practiced on a variety of oxidatively bleached pulps, but is especially useful on elemental chlorine free (ECF) and totally chlorine free (TCF) kraft pulps. In its broadest aspect, the method of this invention may be practiced by adding
20 from .1 - 3.0% by weight (based on the oven-dried weight of the pulp) of a treating agent selected from the group consisting of hydrosulfite, (such as zinc hydrosulfite or sodium hydrosulfite) formamidine sulfinic acid (FAS), and a sulfoxylate (such as sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate and acetaldehyde sulfoxylate)
25 to the pulp as a final stage (except for washing) using

selected pH, temperature and retention times. Sodium hydrosulfite is preferred, especially for environmental reasons.

The addition of the treating agent is preferably done
5 as a solution of the treating agent and may be done by any suitable method such as is practiced by those skilled in the art. The pH of the pulp is maintained between 4.5 and 13 and the temperature of the pulp is maintained between 50 and 100 degrees C. The retention time is from 30 minutes
10 to 6 hours.

In a further refinement of this invention, additional strength enhancement may be achieved by adding a selected quaternary ammonium compound or alkoxylated amine to the pulp solution at any time during the chemical processing of
15 the pulp.

Detailed Description of the Invention and Description of the Preferred Embodiment

20 The present invention provides a method for increasing the physical strength of oxidatively bleached wood pulp which has been made using kraft processes. The method comprises treating the pulp as a final stage with a member selected from the group consisting of hydrosulfite,
25 formamidine sulfinic acid (FAS), and a sulfoxylate (such as sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate and acetaldehyde sulfoxylate). A hydrosulfite

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is preferred, such as one selected from the group consisting of sodium hydrosulfite and zinc hydrosulfite (especially sodium hydrosulfite). For the treating agent, a level of .1 - 3.0% of addition based on the oven-dried weight of the pulp is used, and the solution containing pulp and treating agent should be processed, at a temperature of 50 - 100 degrees C, a pH of 4.5 - 13, and most conveniently for a retention time of .5 - 6 hours. The treating agent is preferably used in the form of a solution added to the pulp slurry. Improvements in strength as measured by tensile tests show increases over 9.0% and more particularly in the range of 9.9 to 30.2%. Improvements in strength as measured by tear tests show increases over 25% and more particularly in the range of 27.1 - 39.5%.

If hydrosulfite is used the general conditions above apply. However, for sodium hydrosulfite (SHS) further refinements of the invention are as follows: minimum requirements are an addition level of .1 - .5% for SHS, pH = 4.5 - 6, temperature = 50 - 60 degrees C, and a retention time = .5 - 1 hour. Better results with SHS may be obtained with .5 - 1.5% SHS, pH = 6.0 - 8.0, temperature = 70 - 80 degrees C, and a retention time = 1 - 2 hours. Preferred conditions for use of SHS are 1.5 - 3% SHS, pH = 7 - 9, temperature = 80 - 95 degrees C, and a retention time = 2 - 4 hours.

If FAS is used as the treating agent the percent of addition is from .1 - 3.0% based on the oven-dried weight of the pulp, but it is preferred that the pH is selected to be from 5.5 - 13.0, the retention time is selected to be from 30 minutes - 4 hours, and the temperature is selected to be 60 - 100 degrees C.

If sulfoxylates are used, the percent addition is from .1 - 3.0% based on the oven-dried weight of the pulp, but it is preferred that the pH is selected to be 4.5 - 13.0, the retention time is selected to be 30 minutes - 6 hours, and the temperature is selected to be 55 - 100 degrees C.

In more particular terms, the process parameters will also vary according to the type of pulp that is being used. In the case of TCF kraft pulp to be treated with hydrosulfite, it is preferred that the pH be maintained between 6.5 and 8.5, the temperature of the pulp be between 80 and 95 degrees C., the dosage of hydrosulfite be between .5 and 1.5 %, and the retention time be between 1 and 4 hours.

In the case of recycled, oxidatively bleached, kraft color ledger, it is preferred that the pH be maintained between 6.5 and 8.5, the temperature of the pulp be between 65.0 and 85.0 degrees C, the dosage of hydrosulfite be between .5 and 1%, and the retention time be between .5 and 1.5 hours.

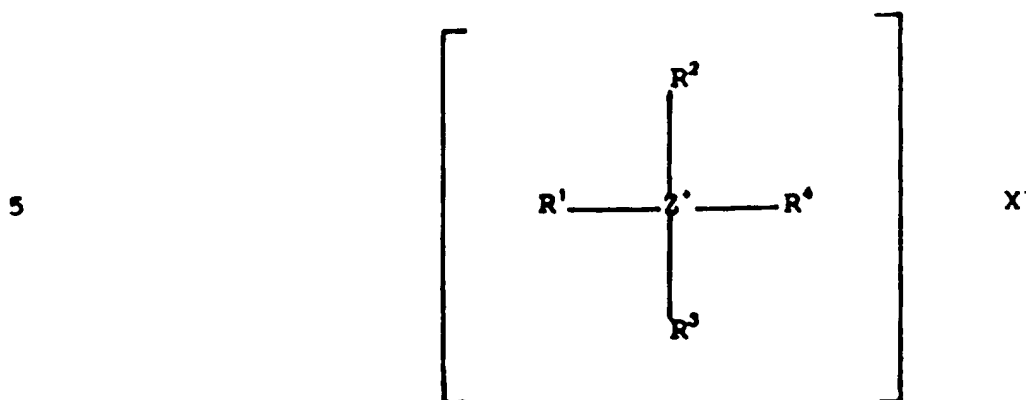
While there are a number of ways in which to practice this invention in the context of a multistage treatment sequence, it is critical that the hydrosulfite stage be the final chemical treatment (not counting water washes).

5 The solution containing pulp and treating agent may also contain one or more of the following: a chelate such as ethylenediaminetetracetic acid (EDTA), sodium tripolyphosphate (STPP), diethylenetriaminepentacetic acid (DTPA), N-(hydroxymethyl)-ethylenediaminetriacetic acid
10 (HEDTA), triethanolamine (TEA), nitrilotriacetic acid (NTA); a phosphonic acid chelate such as diethylenetriaminepenta(methylenephosphonic) acid (DTPMP); an alkali such as sodium hydroxide, sodium carbonate or calcium hydroxide; and a quaternary ammonium compound or
15 alkoxylated amine as described below.

In a particular refinement of this invention, a kraft pulp treated by at least one oxidative step (for example ozone, oxygen or hydrogen peroxide) is treated with a member selected from the group consisting of

20 (I) a quaternary ammonium compound selected from the group consisting of

(a) compounds of Formula I:



Formula I

10

wherein:

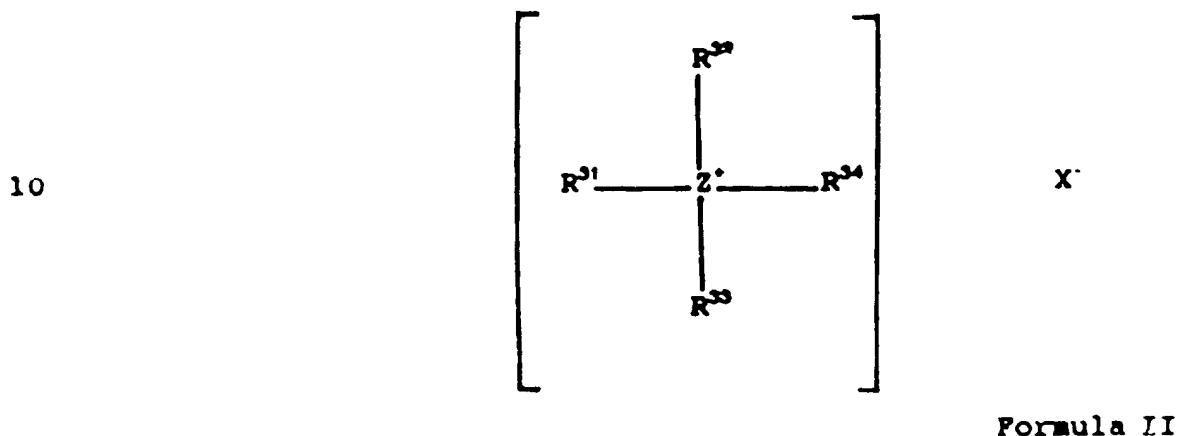
one of R^1 , R^2 , R^3 and R^4 is selected from the group consisting of C_{14} - C_{22} alkyl and C_{14} - C_{22} alkenyl, wherein the
 15 alkyl or alkenyl optionally contains one to three substituents selected from methyl and ethyl (especially methyl);

the remaining R groups are each independently selected from the group consisting of C_1 - C_4 straight chain alkyl,
 20 $-(\text{C}_2\text{H}_4\text{O})_x\text{H}$ and $-(\text{C}_3\text{H}_6\text{O})_x\text{H}$ where x = a number from 1 to 4 inclusive;

Z is selected from the group consisting of nitrogen and phosphorous, preferably nitrogen; and

X⁻ is selected from the group consisting of any suitable and convenient anion (for example, X⁻ is selected from the group consisting of CO₃⁻², HCO₃⁻¹, PO₄⁻³, HPO₄⁻², H₂PO₄⁻¹, OH⁻¹, F⁻¹, Br⁻¹, Cl⁻¹, I⁻¹, HSO₃⁻¹, HSO₄⁻¹, SO₄⁻², SO₃⁻², S₂O₄⁻², CH₃CO₃⁻¹ and CH₃SO₄⁻¹);

(b) compounds of Formula II wherein:



15

wherein:

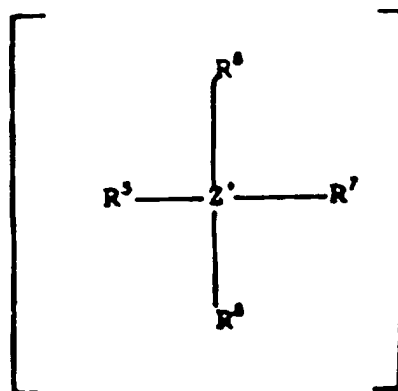
two of R³¹, R³², R³³ and R³⁴ are selected independently from the group consisting of C₁-C₂₂ straight chain alkyl and C₆-C₂₂ alkenyl, wherein the alkyl or alkenyl optionally contains one to three substituents selected from methyl and ethyl (especially methyl);

the remaining R groups are each independently selected from the group consisting of C₁-C₄ straight chain alkyl and -(C₂H₄O)_xH and -(C₃H₆O)_xH where x = a number from 1 to 4 inclusive; and

Z has the same meaning as defined under Formula I.

(c) compounds of Formula III:

5

 HSO_4^-

Formula III

10

wherein:

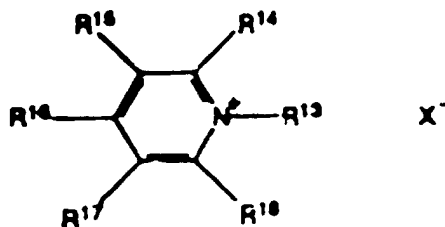
R^5 , R^6 , R^7 and R^8 are each independently selected from the group consisting of C_1 - C_6 ; and

15

Z has the same meaning as defined for Formula I;

(d) a pyridinium salt of Formula IV:

20



Formula IV

25

wherein:

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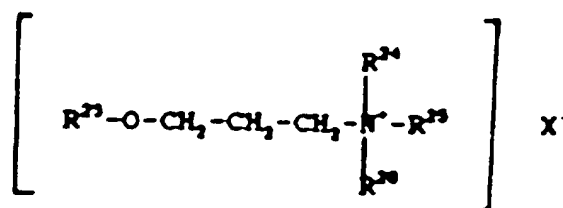
R^{13} is selected from the group consisting of $C_{14}-C_{22}$ alkyl and $C_{14}-C_{22}$ alkenyl, wherein the alkyl or alkenyl optionally contains one to three substituents selected from methyl and ethyl (especially methyl);

5 the remaining R groups are each independently selected from the group consisting of hydrogen, C_1-C_3 straight chain alkyl; and

X' has the same meaning as described in Formula I;

(e) compounds of Formula V:

10



15

Formula V

wherein:

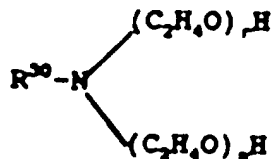
R^{23} is selected from the group consisting of C_8-C_{14} alkyl and C_8-C_{14} alkenyl, where the alkyl and alkenyl optionally (but not preferably) have one to three substituents selected from methyl and ethyl (especially methyl); and

20 each of R^{24} , R^{25} , and R^{26} are independently selected from the group consisting of C_1-C_4 alkyl, C_7-C_8 alkenyl, $(CH_2-CH_2-O)_nH$ and $(CH_2-CH_2-CH_2-O)_nH$ where n = a number from 1 to 4 inclusive;

and

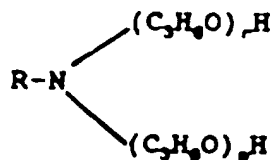
(II) an alkoxyated amine selected from ethoxylated amines of Formula VI and propoxylated amines of Formula VII:

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Formula VI



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Formula VII

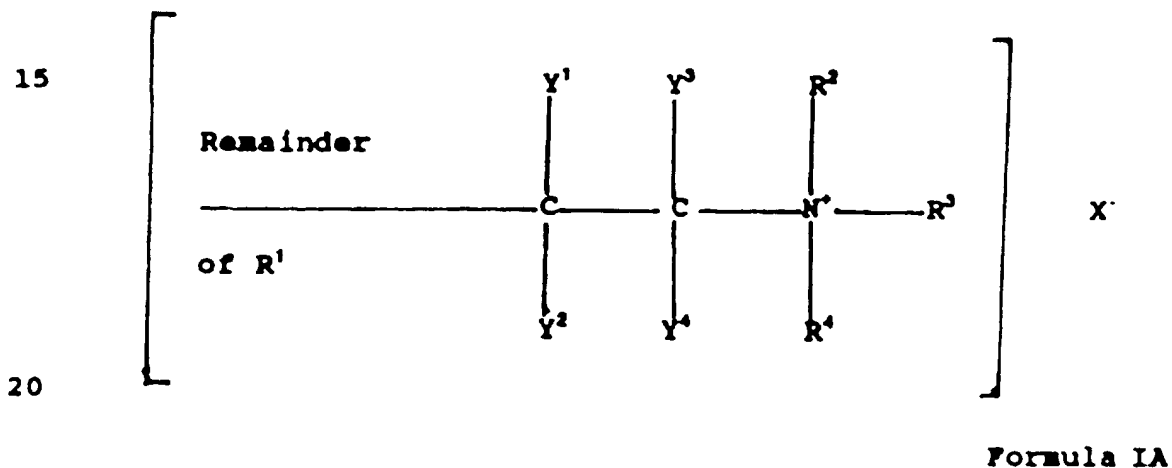
wherein R^{30} is a member of the group consisting of straight chain alkyls having 8 to 22 carbons, optionally having one to three substituents selected from methyl and ethyl (especially methyl); and r and p each stand for integers such that r and p each must have a value of at least one, are selected independently, and the sum of $r + p$ is a number from two to 12 inclusive.

25 For any of the R groups listed in Formulas I through V, any carbon atom (a) attached to the nitrogen or phosphorous, (b) adjacent to the nitrogen or phosphorous or

(c) next adjacent to the nitrogen, may also be substituted by one or more electron withdrawing groups such as chlorine, fluorine, CH_2F and CF_3 , provided that chlorine and fluorine are not attached to the nitrogen or phosphorous.

5 Such compounds would include those having only one electron-withdrawing group as well as those with multiple substitutions with such groups. Examples of those having multiple electron-withdrawing groups include the following wherein each of the Y designations indicates sites where
10 electron withdrawing groups such as the ones described above may be used:

(a) compounds of Formula IA:



wherein R^1 , R^2 , R^3 and R^4 have the meanings described for Formula I, and each of the Y substituents are independently
25 selected from the group consisting of chlorine, fluorine, CH_2F and CF_3 ;

(b) compounds of Formula I in which at least one of R^2 , R^3 and R^4 is independently selected from the group consisting of CH_2F and CF_3 ;

(c) compounds of Formula II in which at least one of R^{32} , R^{33} and R^{34} is independently selected from the group consisting of CH_2F and CF_3 ; and

(d) compounds of Formula IV in which at least one of R^{14} - R^{18} is selected from the group consisting of chlorine, fluorine, CH_2F and CF_3 . Octadecyltrimethylammonium bromide and cetyltri-methylammonium bromide are particular examples of quaternary ammonium compounds which are useful in practicing the invention.

The quaternary or alkoxylated compounds may be added at any stage prior to or at the same time that the treating agent is added. The amounts and methods of adding such quaternary ammonium compounds or alkoxylated amines are as follows.

For quaternary ammonium compounds -

The addition of at least one quaternary compound of the Formulae described above is accomplished by one of the following methods:

(a) Quaternary compound is added to the treating solution -

(1) The quaternary compound is dissolved in water at a level of from 1 to 50 percent based on the weight of the treating agent to be used.

(2) The pH is adjusted to 10 with NaOH or Na₂CO₃.

(3) The treating agent is added to the solution (and dissolved if a solid).

(b) Quaternary compound is blended with the treating agent -

5

(1) At least one quaternary compound is mixed with the selected treating agent in a ratio of from about 1 percent to about 50 percent based on the weight of the treating agent used.

10

(2) The blended mixture is then added to the pulp slurry which has been prepared as described above.

(c) Quaternary compound is added at the same time the treating agent is added -

15

(1) At least one quaternary compound is added to the pulp slurry which has been prepared as described above.

(2) The addition of the quaternary compound is done at about the same time the treating agent is added to the pulp slurry.

20

The addition levels of quaternary compound are in the range of 1 to 50 percent based on the weight of the treating agent used. For one ton of fiber (oven-dried basis), this means that about 5 - 40 pounds (2.3 - 18.2 kg) are used.

25

For alkoxylated amines -

For example, the addition of the alkoxylated amine may be accomplished by one of the following methods:

(a) An amine compound of Formula VI or VII is added
5 to the treating agent solution -

- (1) The amine compound is dissolved in water.
- (2) The pH is adjusted to 10 with NaOH or Na_2CO_3 .
- (3) The treating agent is added and dissolved.

(b) An amine compound of Formula VI or VII is blended
10 with the treating agent -

- (1) At least one amine compound is mixed with the selected treating agent.
- (2) The blended mixture is then added to the pulp slurry which has been prepared as
15 described above.

(c) An amine compound of Formula VI or VII is added at the same time the treating agent is added -

- (1) At least one amine compound is added to the pulp slurry which has been prepared as
20 described above.
- (2) The addition of the amine compound is done at about the same time the treating agent is added to the pulp slurry.

The amount of amine compound added is from about 5
25 pounds (2.3 kilograms) (0.25 percent addition level) to about 20 pounds (9.1 kilograms) (1.0 percent addition level) per ton of dry fiber content with:

- (a) 2 - 60 pounds (.91 - 27.2 kg) of hydrosulfite;
- (b) 2 - 60 pounds (.91 - 27.2 kg) of FAS;
- (c) 2 - 60 pounds (.91 - 27.2 kg) of sulfoxylate.

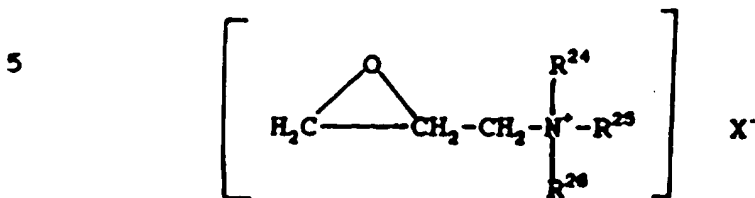
Quaternary ammonium compounds as described above may
5 be obtained as follows.

The compounds of Formulae I, II and III where Z =
nitrogen may be made by methods well known to those skilled
in the art such as by alkylation of a tertiary amine, or
sometimes purchased commercially.

10 For compounds of Formula I where Z = phosphorous, some
of these compounds may be purchased commercially. Others
may be made by methods known to those skilled in the art.
For example, the methods described in Organic Reactions,
Volume 14 (John Wiley & Sons, Inc. 1987) at pages 388-393
15 (incorporated by reference herein) describe such methods,
except that the appropriate trialkylphosphine would be used
instead of the triphenyl material described.

The compounds of Formula IV may be made in the same
manner as compounds of Formulae I and II except that the
20 starting material is pyridine or a substituted pyridine.

The compounds of Formula V may be made by reacting a primary alcohol of formula R^{23} -OH with a quaternary amine propyl epoxide of Formula VI:



Formula VI

10

under alkaline conditions. The reaction scheme is as follows:

alcohol + epoxide $\xrightarrow{40^\circ \text{C}/\text{NaOH}/\text{pH}=10}$ Compound of Formula V

15

It is also to be noted that in selecting quaternary compounds to be used in this invention, mixtures of quaternary compounds may be used. These mixtures may be made by blending different quaternary compounds together or may be found in the products itself. Synthetic or natural materials may be used. For example, for the longer chain alkyl groups, a mixture of chain lengths such as may be found in the chain distribution naturally occurring in materials such as tallow, lard, soybean, coconut, tall oils and products from petroleum cracking towers may be used. Additionally, synthetic fatty materials may also be used when compounds having a specific chain length are desired.

In general, fats may be saponified, the reaction products skimmed off and acidified. The fatty acid thus formed may be subjected to an amination reaction such as the Schmidt reaction to form the quaternary compound. (A description of the Schmidt reaction may be found in C. R. Noller, Textbook of Organic Chemistry (W. B. Saunders Co., 1966) at page 224, incorporated by reference herein.

The selected alkoxyated amines may be obtained as follows.

10 The compounds of Formulae VI and VII may be made by methods well known to those skilled in the art or sometimes purchased commercially. Such methods include heating (if it is a solid) the appropriate alkyl amine or natural mixtures such as tallow or coco amine until it becomes a liquid and then adding sodium hydroxide at a level of about 0.1% based on the weight of the amine. Ethylene oxide or propylene oxide is then added in an ethoxylation or propoxylation reaction to form the desired compound of Formula VI or VII.

20 Strength is conveniently measured in terms of tensile tests and tear tests. In general, the process of this invention may be practiced to give increases of over 9% for tensile strength and increases of 25 to 35% for tear strength. Note that Breaking Length = 3658 (tensile strength/mass per unit area).

25

Tensile Test

Handsheets were prepared in accordance with Technical Association of Pulp and Paper Industry (TAPPI) Standard Method T 205 om-88 (incorporated by reference in its entirety herein) except that instead of .3% consistency in Section 7.1.2, .2% consistency was used in accordance with note 3 of 7.1.2 to make the handsheets. Test specimens were prepared from these handsheets using TAPPI Standard Method T 220 om-88 incorporated by reference in its entirety herein. The tensile test was performed according to TAPPI Standard Method T 494 om-88 incorporated by reference in its entirety herein. This T 494 method is used to evaluate the tensile breaking properties of paper and paperboard using constant rate of elongation apparatus (Instron 4301). Tensile strength is measured in kilonewtons per meter (kN/m). Breaking length is calculated from the tensile strength, and is defined as the length in meters of a strip of paper one inch wide which, when suspended vertically by one end, will break from its own weight. The control was handsheets prepared by the same TAPPI methods described in this paragraph, but which were not treated with any hydrosulfite. All of the TAPPI Standard Methods described in this paragraph are incorporated by reference in their entirety herein.

Tear Test

Test specimens were prepared as described under the description of Tensile Test using TAPPI Standard Method T 205 om-88 (with .2% consistency) and TAPPI Standard Method T 220 om-38. Tear tests were performed according to TAPPI Standard Method T 414 om-88 incorporated by reference in its entirety herein. This procedure measures the internal tearing resistance of paper using an Elmhendorf type apparatus (TMI 93-11-00 from Testing Machines Incorporated, Amityville, New York). The control was handsheets prepared by the same TAPPI methods described in this paragraph, but which were not treated with any hydrosulfite.

15

EXAMPLES

The following Examples are illustrative of the invention but should not be construed as limitations thereon. Unless otherwise indicated, all chemical symbols and abbreviations (ml. g, kg, and so forth) have their usual and customary meanings and temperatures are in degrees Centigrade. Unless otherwise indicated, all percents are weight percents. The percent of hydrosulfite used is based on the oven-dried weight of the pulp.

25

Pulp 1-1 - TCF softwood kraft pulp treated with oxygen, chelate and hydrogen peroxide (not necessarily in that order) and having an International Organization of Standardization (ISO) brightness of 68%.

- 5 Pulp 1-2 - TCF softwood kraft pulp treated with oxygen, chelate and hydrogen peroxide (not necessarily in that order) and having an ISO brightness of 78%.

Pulp 2-1 - TCF softwood kraft pulp treated with oxygen, chelate and hydrogen peroxide (not necessarily in that
10 order) and having an ISO brightness of 65%.

Pulp 3-1 - Pulp was made from colored ledger waste paper. To 2.27 kg (5 lb) of colored broke was added 20.7 liters of water at 65 degrees C in a lab pulper (Adirondack Machine Company, Glen Falls, New York). Repulping was carried out
15 over a period of 15 minutes.

EXAMPLE 1

(Blank)

A sample of Pulp 1-1 was used to make 5 handsheets
20 according to TAPPI Standard Method T 205 om-88 and tensile strips were made according to TAPPI Standard Method T 220 om-88, except that the pulp was diluted to .85% and disintegrated for 43,850 revolutions. In accordance with note 8 of Method T 205, after disintegration, the pulp was
25 diluted to .2% for preparation of the physical test handsheets. The tensile strength and breaking length

values were obtained in accordance with TAPPI Standard Method T 494 om-88 and the values are recorded in Table I. These values represent the average of 9 tests.

5

EXAMPLE 2

(AP Treatment)

A sample of Pulp 1-1 was treated with an acid wash (A) followed by a hydrogen peroxide stage (P). In the acid wash the consistency of the pulp was adjusted to 3% with a 2.0% sulfuric acid (160 g of oven-dried pulp diluted with 5173 ml of 2% sulfuric acid) and allowed to stir for 30 minutes at room temperature (25 degrees C). After the 30 minutes, the pulp was dewatered to a consistency of 15-20% using a 200 mesh American Standard Test Method (ASTM) sieve with 172-207 kPa (25-30 lb) of pressure, and washed once with 5 liters of deionized water. The consistency of the pulp was then adjusted to 12% with deionized water for the peroxide stage. The P stage was carried out at 80 degrees Celsius at an ending consistency of 10%, and a retention time of 30 minutes. All 155 g of oven-dried pulp were bleached in a single plastic bag. Heating was achieved with a hot water bath, and stirring was accomplished in a Hobart Planetary Action Mixer. Bleach solution (60 ml containing 2.5% hydrogen peroxide, 1.0% sodium hydroxide, .5% diethylenetriaminepentaacetic acid (DTPA) and 3% sodium silicate was slowly added using a 60 ml syringe. After the bleach solution was added 198 ml of deionized water was

added to bring the pulp to a consistency of 10%. The pulp was then placed back into the hot water bath. After a retention time of 90 minutes, residual hydrogen peroxide was removed by the addition of sulfurous acid to a pH of 4.5. Hydrogen peroxide removal was confirmed by using "Baker Test Strips for Hydrogen Peroxide" from J. T. Baker Incorporated. The pulp was stored at 5 degrees C until physical testing was begun. Five handsheets were made from this pulp using the procedure described in Example 1. The tensile strength and breaking length value in Table 1 are the average of 8 tests.

EXAMPLE 2

(APVEY Treatment)

A sample of Pulp 1-1 was treated with an acid wash and a hydrogen peroxide stage as described in Example 2. Following this AP treatment, the pulp was treated with a hydrosulfite/NaOH extraction/hydrosulfite sequence (also called a Y E Y sequence where Y=sodium hydrosulfite and E=NaOH extraction). The Y stages were conducted in a Quantum High Shear Mixer, model Mark IV. For the first Y stage the pulp (77.5 g oven-dried pulp) was diluted to 5% consistency with deionized water. This 5% pulp slurry was then preheated to 80 degrees C in the 2 liter bowl of the Quantum mixer. The pH of this pulp of 5% consistency was then adjusted to 5.5 by adding dilute sulfuric acid with a syringe through the bowl cover septum. A vacuum was then

pulled on the bowl for 30 seconds. After 30 seconds of vacuum, the displaced air was replaced by nitrogen gas. This sequence was repeated 3-5 times to remove all oxygen trapped in the pulp slurry. After the final vacuum, enough
5 nitrogen gas was added to the bowl to maintain a slightly positive pressure throughout the retention time of four hours. Following the final addition of nitrogen gas, 20 ml of .75% sodium hydrosulfite (based on the oven-dried weight of the pulp) was added as a solution (20 ml volume).
10 During the addition of the sodium hydrosulfite bleach solution, the pulp was mixed at 15 Hertz (600 revolutions per minute (rpm)) for 30 seconds. After this mixing was finished the pulp was then mixed for 8 seconds at 50 Hertz (2400 rpm). Next the pulp was mixed at 15 Hertz for 4
15 seconds every minute during the entire retention time. After a 4 hour retention time, the pulp was removed from the bowl for a NaOH extraction stage. The NaOH extraction (E stage) was performed by adjusting the pH of the pulp to 12.0 using 10% NaOH solution. The resulting pulp slurry
20 was mixed at room temperature (25 degrees C) for 30 minutes. After 30 minutes, the pulp was dewatered to a consistency of 15-20% using a 200 mesh ASTM sieve and a vacuum. The pulp was then washed by adding 1000 ml of deionized water and mixing the slurry for 2 minutes. The
25 pulp was then dewatered as described above. The second sodium hydrosulfite stage was performed using the same procedure as described for the first Y stage. A sample of

pulp (67 g of oven-dried pulp diluted to 5% consistency with deionized water) was adjusted to a pH of 11.0 by adding 10% NaOH. The resulting slurry was then treated as described above to remove the entrained oxygen and a 1% solution of sodium hydrosulfite was added. The retention time for this second Y stage was 15 hours. All other conditions were the same as described for the first Y stage of this Example. The pulp was stored at 5 degrees C until physical testing was begun. Five handsheets were made and data was collected as described in Example 1. The data is recorded in Table I and represents the average of 9 tests.

EXAMPLE 4

(Blank)

Twenty handsheets were made from a sample of Pulp 1-2 (1.2 g oven-dried pulp/handsheet) as received from the mill using TAPPI Standard Method T 205 om-88 and tensile test strips were made according to TAPPI Standard Method 220 ca-88. In accordance with note 3 of TAPPI Standard Method T 205 om-88, after disintegration the pulp was diluted to .2% consistency for preparation of the physical test handsheets. The tensile strength and breaking length values in Table I represents the average of 36 tests which were done on 20 handsheets.

EXAMPLE 5

(Y Treatment)

A sample of Pulp 1-2 was treated with sodium hydrosulfite according to the following procedure. Pulp
5 (12 g oven-dried pulp diluted to 3% consistency with deionized water) was allowed to stand for 15 hours. The pulp slurry was then disintegrated for 15,000 revolutions at room temperature. The consistency of the pulp was adjusted to 3.5% by removing 57 ml of water. The resulting
10 pulp slurry was placed in a 500 ml wide mouth polypropylene bleaching bottle. The bottle was heated to 73 degrees C using a hot water bath. The bottle was then transferred to a deaeration station equipped with vacuum and nitrogen supply. The pulp was deaerated by alternately subjecting
15 the bottle to a vacuum and then flushing the bottle with nitrogen. This process was repeated three times. Each bottle was then moved to a mixing station consisting of a rubber stopper attached to a ring stand through which stopper was mounted an overhead variable speed mixer, a pH
20 probe, and a nitrogen line. The rubber stopper also contained an opening through which bleach could be added with a syringe. Mixing was started and the pH was adjusted to the desired pH of 8.0 with .1 N sodium hydroxide as required. Sodium hydrosulfite (1.3% based on weight of
25 oven-dried pulp) was then added as a solution by buret. After mixing for 3 minutes and subjecting it to another vacuum/nitrogen sequence, the bottle was recapped and

returned to the hot water bath for a 113 minute retention time. The pulp was then removed from the water bath. Handsheets from this pulp slurry were made according to TAPPI Standard Method T 203 om-88. Tensile specimens were
5 made according to TAPPI Standard Method T 230 om-88. The tensile test was done according to TAPPI Standard Method T 494 om-88. The data is recorded in Table I and is the average of 10 tests done on 5 handsheets.

10

EXAMPLE 6

(Y Treatment)

A sample of Pulp 1-2 was treated with sodium hydroxulfite according to the following procedure. Pulp
(12 g oven-dried pulp diluted to 3% consistency with
15 deionized water) was allowed to stand for 15 hours. The pulp slurry was then disintegrated for 15,000 revolutions at room temperature. The consistency of the pulp was adjusted to 3.5% by removing 57 ml of water. The resulting pulp slurry was placed in a 500 ml wide mouth polypropylene
20 bleaching bottle. The bottle was heated to 68 degrees C using a hot water bath. The bottle was then transferred to a deaeration station equipped with vacuum and nitrogen supply. The pulp was deaerated by alternately subjecting the bottle to a vacuum and then flushing the bottle with
25 nitrogen. This process was repeated three times. Each bottle was then moved to a mixing station consisting of a rubber stopper attached to a ring stand through which

stopper was mounted an overhead variable speed mixer, a pH probe, and a nitrogen line. The rubber stopper also contained an opening through which bleach could be added with a syringe. Mixing was started and the pH was adjusted to 9.0 with .1 N sodium hydroxide as required. Sodium hydrosulfite (.9% based on weight of oven-dried pulp) was then added by buret. After mixing for 3 minutes and subjecting it to another vacuum/nitrogen sequence, the bottle was recapped and returned to the hot water bath for a 146 minute retention time. The pulp was then removed from the water bath. Handsheets from this pulp slurry were made according to TAPPI Standard Method T 205 om-88. Tensile specimens were made according to TAPPI Standard Method T 220 om-88. The tensile test was done according to TAPPI Standard Method T 494 om-88. The data is recorded in Table I and is the average of 10 tests done on 5 handsheets.

EXAMPLE 7

20

(Blank)

A sample of Pulp 2-1 was used to make handsheets in accordance with TAPPI Standard Method T 205 om-88 and tensile test strips according to TAPPI Standard Method T 220 om-88 except that the pulp was diluted to a consistency of .25% and was disintegrated for 43,850 revolutions. In accordance with note 8 of TAPPI Standard Method T 205 om-88, after disintegration the pulp was diluted to .2%

consistency for preparation of the physical test handsheets. The tensile strength and breaking length data are recorded in Table I and the data represents the average of 9 tests done on 5 handsheets.

5

EXAMPLE 8

(APEYWY Treatment)

A sample of Pulp 2-1 was treated with an acid wash followed by a hydrogen peroxide stage. In the acid wash
10 the consistency of the pulp was adjusted to 5% with a 2.0% sulfuric acid solution (103 g of oven-dried pulp at 12.4% consistency was diluted with 1256 ml of 2% sulfuric acid) and the mixture was stirred for 30 minutes at room temperature (25 degrees C). The pulp was then dewatered to
15 a consistency of 15-20% using a 200 mesh ASTM sieve with 172-207 kPa (25-30 lb) of pressure, and washed once with 2 liters of deionized water. The consistency of the pulp was then adjusted to 12% with deionized water for the hydrogen
oxide stage. The P stage was carried out at 80 degrees
20 Celsius, at for a retention time of 90 minutes. The final consistency was 10%. A sample of the pulp (95 g oven-dried weight) was divided into 2 parts (47.5 g each) and placed into plastic bags. The bags were preheated to a temperature of 80 degrees C with a hot water bath. Each
25 bag was then emptied individually into the bowl of a Hobart Planetary Action Mixer N-50 (Hobart Corporation, Troy, Ohio) and mixed with 70 ml of bleach solution containing

2.5% hydrogen peroxide, 1.0% NaOH, .5% DTPA and 3% sodium silicate. The addition of these material was accomplished slowly with a 60 ml syringe. After the bleach solution was added 9.2 ml of deionized water was added to each bag to bring the pulp to a 10% consistency. After mixing, the solutions were placed back into the bags and the bags were placed back into the water bath. After a retention time of 90 minutes, residual hydrogen peroxide was removed by the addition of sulfurous acid sufficient to obtain a pH of 4.5. Hydrogen peroxide removal was confirmed using the Baker test strips described in Example 2. The pulp was stored at 5 degrees C until physical testing was begun. After the P stage the samples were combined and a ZYWW sequence was used to treat the sample (where Z and Y have been previously defined and W = washing step. For the first Y stage the pulp (81 g oven-dried basis) was diluted to 5% consistency with deionized water. This pulp slurry was then preheated to 80 degrees C in the 2 liter bowl of a Quantum mixer. The pH of this hot slurry was then adjusted to 10.0 by adding dilute NaOH through the septum covering the bowl. A vacuum was then pulled on the bowl for 30 seconds. Next, the displaced air was replaced by nitrogen gas. This sequence was repeated 3-5 times to remove all oxygen trapped in the pulp slurry. After the final vacuum, enough nitrogen gas was added to maintain slightly positive pressure throughout the retention time of 2 hours to prevent air from re-entering the bowl.

Following the final addition of nitrogen gas, sodium hydrosulfite (.75% by weight based on the oven-dried weight of pulp) was added as a solution (20 ml volume) using the mixing procedure described in Example 3. After a 2 hour retention time the pulp was removed from the bowl for the washing stage. In the W stage, 67 g of oven-dried pulp was diluted to 5% consistency with deionized water. The pulp was then dewatered to 15-20% consistency using a 200 mesh ASTM sieve. This dilution/dewatering sequence was repeated twice. Next the second Y stage was performed using the same procedure described above for the first Y stage. The pulp was then stored at 5 degrees C until physical testing was begun. Handsheets were made with the pulp according to TAPPI Standard Method T 205 om-88 and tensile strength strips were made according to TAPPI Standard Method T 220 om-88. The procedure was slightly altered, however, so that the pulp was diluted to a consistency of .81% and disintegrated for 43,850 revolutions. In accordance with note 8 of the T 205 method, after disintegration the pulp was diluted to .2% for preparation of the physical test handsheets. The breaking length and tensile strength data are recorded in Table I and represents the average of 9 tests done on 5 handsheets.

EXAMPLE 9

(Blank)

A sample of Pulp 3-1 was used to make handsheets using TAPPI Standard Method T 205 om-88. Tensile specimens were made using TAPPI Standard Method T 220 om-88 and tensile testing was done using TAPPI Standard Method T 494 om-88. Breaking length data is recorded in Table I. The data is the average of 6 tests done on 3 handsheets.

10

EXAMPLE 10

(Y Treatment)

Pulp 3-1 (15 g oven-dried fiber diluted to 4% consistency) was placed in a 500 ml wide mouth polypropylene bottle. The bottle was heated to 65.5 degrees C using a hot water bath. The bottle was then transferred to a deaeration station equipped with vacuum and a nitrogen supply. The pulp was deaerated by alternating between subjecting the bottles to vacuum and then flushing the bottles with nitrogen. This process was repeated three times. The bottle was then moved to a mixing station consisting of a rubber stopper attached to a ring stand through which stopper was mounted an overhead variable speed mixer, a pH probe and a nitrogen line. The rubber stopper also contained an opening through which bleach could be added with a syringe. Mixing was started and the pH was adjusted to the desired pH of 7.0 with .1 N NaOH or .1 N sulfuric acid as required. Sodium

hydrosulfite (1.5% by weight based on the oven-dried weight of the pulp) was then added as a solution (10 ml volume) by syringe. Stirring was continued for 3 minutes, after which each bottle was recapped and returned to the hot water bath for one hour. The pulp was then removed from the water bath. Handsheets from this pulp slurry were made using the procedure described in TAPPI Standard Method T 205 om-88. Tensile specimens were made according to TAPPI Standard Method T 220 om-88 and tensile testing was done using TAPPI Standard Method T 494 om-88. The data for breaking length is recorded in Table I. This process was repeated 6 times and the data in Table I is the average of 63 tests.

EXAMPLE 11

(Y Treatment with Octadecyltrimethylammonium Bromide)

The procedure of Example 10 was repeated except that octadecyltrimethylammonium bromide (.75% by weight based on the weight of oven-dried pulp) was added as a solution (10 ml volume) to the pulp slurry just prior to the addition of sodium hydrosulfite. Handsheets were made and testing was done as described in Example 10. The procedure was repeated 2 times. The data is recorded in Table I and represents the average of 10 tests.

EXAMPLE 12

(Y Treatment with Cetyltrimethylammonium Bromide)

The procedure described in Example 11 was repeated except that cetyltrimethylammonium bromide (.75% by weight
5 based on the weight of oven-dried pulp) was added as a solution (10 ml volume) was used instead of the octadecyltrimethylammonium bromide. The procedure was repeated 6 times. The data is recorded in Table I and represents the average of 53 samples.

10

TABLE I

Tensile Test Results

Example	Description	Breaking Length (Meters)	Tensile Strength kN/m
5 1	Pulp 1-1 Blank	2793	1.73
2	Pulp 1-1 AP	2925	1.90
3	Pulp 1-1 APYFY	3837	3.52
4	Pulp 1-2 Blank		1.48
5	Pulp 1-2 Y		2.23
10 6	Pulp 1-2 Y		2.13
7	Pulp 2-1 Blank	2933	1.88
8	Pulp 2-1 APZYWY	3262	1.89
9	Pulp 3-1 Blank	4252	2.54
10 10	Pulp 3-1 Y	4672	3.00
15 11	Pulp 3-1 Y (Octadecyl- trimethylammonium bromide)	5486	3.83
12	Pulp 3-1 Y (Cetyltrimethyl- ammonium bromide)	5537	3.58

EXAMPLES 13-17

(Tear Strength)

Pulps 1-1 and 1-2 were evaluated for tear strength. These pulps were bleached using similar TCP sequences as described in the definitions of the pulp above. All pulps were stored at a temperature of 0 degrees C between treatment and testing for tear strength unless otherwise indicated. As usual all percentages are based on weight of oven-dried pulp unless otherwise noted.

10

EXAMPLE 13

(Blank)

A sample of Pulp 1-1 was used to make 15 handsheets using TAPPI Standard Method T 205 om-88 and tear test strips were made using TAPPI Standard Method T 220 om-88. In accordance with note 8 of the T 205 method, after disintegration the pulp was diluted to a consistency of .2% for preparation of the physical test handsheets. The tear strength data is recorded in Table II. The data is the average of 30 tests on these handsheets.

EXAMPLE 14

(Y Treatment)

A sample of Pulp 1-1 as received from a mill (95% consistency) was diluted to 2% consistency with deionized water and put into a refrigerator overnight. The pulp was then disintegrated at room temperature (25 degrees C) for

15 minutes at 27,000 revolutions per minute. Water (6100 ml) was then removed from the pulp using a 200 mesh ASTM sieve to adjust the consistency to 3.5%. Pulp (15 g oven-dried diluted to 3.5% consistency) was put into a 500 ml
5 polypropylene bottle. The pulp was preheated to a temperature of 55 degrees C in a hot water bath. After preheating was completed a vacuum was then pulled on the bottle to remove any trapped air. The displaced air was then replaced by nitrogen gas. This sequence was repeated
10 3 times to remove all oxygen trapped in the pulp slurry. The pulp was then placed in the bleaching apparatus described in Example 10 with a mechanical stirrer. A constant flow of nitrogen gas was maintained over the pulp in the bottle throughout the retention time of 44 minutes
15 to insure that no air would re-enter the bottle. The pH of this hot 3.5% pulp was then adjusted to 9.1 by adding dilute NaOH. Sodium hydrosulfite was added (.6% by weight based on the oven-dried weight of the pulp) was added by buret as a solution with constant vigorous mixing. After
20 a retention time of 44 minutes the pulp was removed from the water bath. The pulp was cooled and stored at 5 degrees C until physical testing was begun. Handsheets were made with this pulp using TAPPI Standard Method T 205 om-88 and tear test strips were made using TAPPI Standard
25 Method T 220 om-88. In accordance with note 8 of the T 205 method, after disintegration, the pulp was diluted to a

consistency of .3% for preparation of the physical test handsheets. The tear strength data is recorded in Table II. The data is the average of 10 tests on 5 handsheets.

5

EXAMPLE 15

(Y Treatment)

A sample of Pulp 1-1 as received from a mill (95% consistency) was diluted to 2% consistency with deionized water and put into a refrigerator overnight. The pulp was then disintegrated at room temperature (25 degrees C) for 10 15 minutes at 27,000 revolutions per minute. Water (6100 ml) was then removed from the pulp using a 200 mesh ASTM sieve to adjust the consistency to 3.5%. Pulp (15 g oven-dried diluted to 3.5% consistency) was put into a 500 ml 15 polypropylene bottle. The pulp was preheated to a temperature of 75.5 degrees C in a hot water bath. After preheating was completed a vacuum was then pulled on the bottle to remove any trapped air. The displaced air was then replaced by nitrogen gas. This sequence was repeated 20 3 times to remove all oxygen trapped in the pulp slurry. The pulp was then placed in the bleaching apparatus described in Example 10 with a mechanical stirrer. A constant flow of nitrogen gas was maintained over the pulp in the bottle throughout the retention time of 21 minutes 25 to insure that no air would re-enter the bottle. The pH of this not 3.5% pulp was then adjusted to 9.1 by adding dilute NaOH. Sodium hydrosulfite (1.1% weight percent

based on the oven-dried weight of the pulp) was added by
buret as a solution with constant vigorous mixing. After
a retention time of 21 minutes the pulp was removed from
the water bath. The pulp was cooled and stored at 5
5 degrees C until physical testing was begun. Handsheets
were made with this pulp using TAPPI Standard Method T 205
om-88 and tear test strips were made using TAPPI Standard
Method T 220 om-88. In accordance with note 3 of the T 205
method, after disintegration, the pulp was diluted to a
10 consistency of .2% for preparation of the physical test
handsheets. The tear strength data is recorded in Table
II. The data is the average of 11 tests on 3 handsheets.

EXAMPLE 16

15

(Blank)

A sample of Pulp 1-2 was processed as described in
Example 4. Tear strength was evaluated as described in the
TAPPI methods described above. The data is recorded in
Table II.

20

EXAMPLE 17

(Y Treatment)

A sample of Pulp 1-2 was processed as described in
Example 6. Tear strength was evaluated as described in the
25 TAPPI methods described above. The data is recorded in
Table II.

TABLE II
Tear Strength

Example	Pulp	Sample	Average Tear (mN)
13	Pulp 1-1	Blank	697.5
14	Pulp 1-1	Y Treatment	886.8
15	Pulp 1-1	Y Treatment	936.5
16	Pulp 1-2	Blank	820.2
17	Pulp 1-2	Y Treatment	1143.8

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for increasing the physical strength of oxidatively bleached pulp which has been made using a kraft process, wherein said method comprises treating the pulp as a final stage with a treating agent selected from the group consisting of hydrosulfite, formamidine sulfinic acid (FAS), and a sulfoxylate selected from the group consisting of formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate and acetaldehyde sulfoxylate, at a level of .1 - 3.0% of treating agent (based on the oven-dried weight of the pulp), at a temperature of 50 - 100 degrees C, and a pH of 4.5 - 13.
2. The method as claimed in Claim 1, wherein the retention time is from 30 minutes to 6 hours.
3. The method as claimed in Claim 1, wherein said treating agent is hydrosulfite.
4. The method as claimed in Claim 1, wherein said hydrosulfite is sodium hydrosulfite.
5. The method as claimed in Claim 3, wherein the pH is maintained between 4.5 and 9.0.

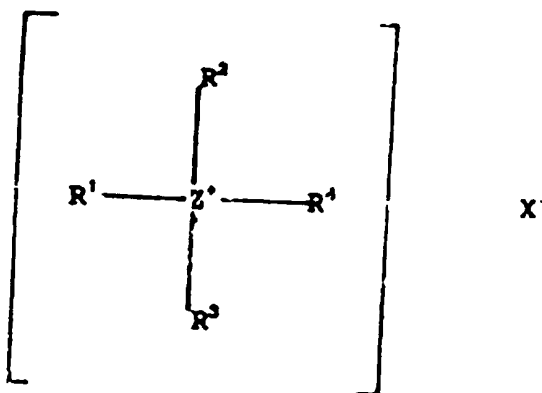
6. The method as claimed in Claim 3, wherein the temperature of the pulp is maintained between 50 and 95 degrees C.
7. The method as claimed in Claim 3, wherein the dosage of hydrosulfite be between .1 and 3.0% by weight.
8. The method as claimed in Claim 3, wherein the dosage of hydrosulfite be between .5 and 3.0% by weight.
9. The method as claimed in Claim 7 wherein said hydrosulfite is sodium hydrosulfite, the addition level is 1.5 - 3%, the pH is 7 - 9, the temperature is 80 - 95 degrees C, and the retention time is 2 - 4 hours.
10. The method as claimed in Claim 1 wherein the treating agent is sodium hydrosulfite used at a level of .5 - 1.5 weight percent based on the oven-dried weight of the pulp, the pH of the solution containing pulp and treating agent is 6.0 - 8.0, the temperature of said solution is 70 - 80 degrees C, and the retention time is 1 - 2 hours.
11. The method as claimed in Claim 1, wherein said pulp is selected from the group consisting of elemental chlorine free pulp and totally chlorine free pulp.

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12. The method as claimed in Claim 1, wherein the treating agent is selected from the group consisting of formamidine sulfinic acid (FAS), sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate and acetaldehyde sulfoxylate.
13. The method as claimed in Claim 1, wherein said treating agent is formamidine sulfinic acid, the pH is from 5.5 - 13.0, the temperature is from 50 - 100 degrees C, and the retention time is from .5 - 4 hours.
14. The method as claimed in Claim 11, wherein said pulp is totally chlorine free pulp, the treating agent is hydrosulfite, the pH is 6.5 - 8.5, the temperature of the pulp is 80 - 95 degrees C, the dosage of hydrosulfite is .5 - 1.5% and the retention time is 1 - 4 hours.
15. The method as claimed in Claim 1 wherein said pulp is recycled kraft color ledger, the pH is maintained between 6.5 and 8.5, the temperature of the pulp is between 65.0 and 85.0 degrees C, the dosage of hydrosulfite is between .5 and 1%, and the retention time is .5 - 1.5 hours.

16. The method as claimed in Claim 1 wherein the solution containing pulp and treating agent contains at least one member selected from the group consisting of:

- (A) a chelate;
- (B) an alkali; and
- (C) a quaternary ammonium compound selected from the group consisting of
- (I) a quaternary ammonium compound selected from the group consisting of
- (a) compounds of Formula I:



Formula I

wherein:

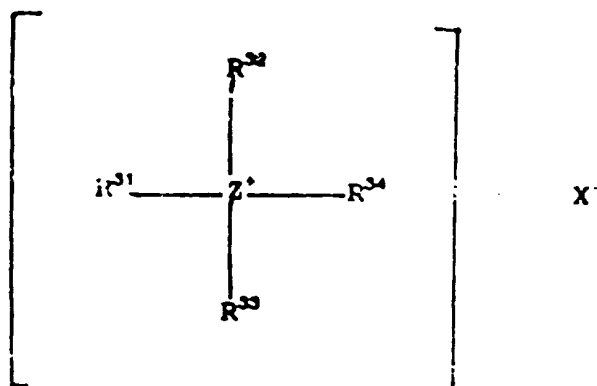
one of R^1 , R^2 , R^3 and R^4 is selected from the group consisting of C_{14} - C_{22} alkyl and C_{14} - C_{22} alkenyl, wherein the alkyl or alkenyl optionally contains one to three substituents selected from methyl and ethyl;

the remaining R groups are each independently selected from the group consisting of C₁-C₄ straight chain alkyl, -(C₂H₄O)_xH and -(C₃H₆O)_xH where x = a number from 1 to 4 inclusive;

Z is selected from the group consisting of nitrogen and phosphorous, preferably nitrogen; and

X⁻ is selected from the group consisting of any suitable and convenient anion (for example, X⁻ is selected from the group consisting of CO₃⁻², HCO₃⁻¹, PO₄⁻³, HPO₄⁻², H₂P₂O₇⁻¹, OH⁻¹, F⁻¹, Br⁻¹, Cl⁻¹, I⁻¹, HSO₃⁻¹, HSO₄⁻¹, SO₄⁻², SO₃⁻², S₂O₄⁻², CH₃CO₃⁻¹ and CH₃SO₄⁻¹);

(b) compounds of Formula II wherein:



Formula II

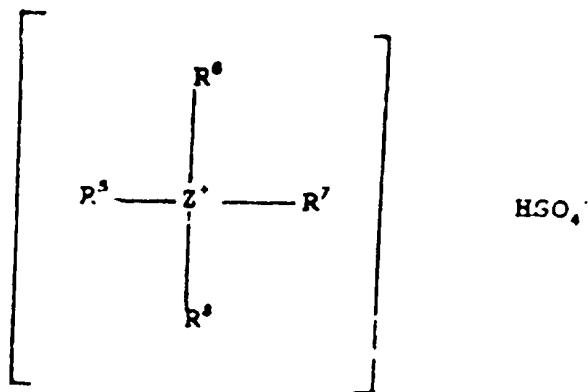
wherein:

two of R^{31} , R^{32} , R^{33} and R^{34} are selected independently from the group consisting of C_1 - C_{22} straight chain alkyl and C_1 - C_{22} alkenyl, wherein the alkyl or alkenyl optionally contains one to three substituents selected from methyl and ethyl;

the remaining R groups are each independently selected from the group consisting of C_1 - C_4 straight chain alkyl and $-(C_2H_4C)_xH$ and $-(C_3H_6C)_xH$ where x = a number from 1 to 4 inclusive; and

Z has the same meaning as defined under Formula I.

(c) compounds of Formula III:



Formula III

wherein:

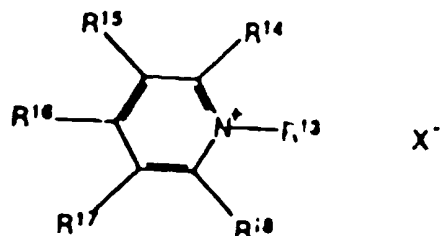
R^5 , R^6 , R^7 and R^4 are each independently selected from the group consisting of C_1 - C_4 ; and

Z has the same meaning as defined for Formula I;

(d) a pyridinium salt of Formula IV:

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Formula IV

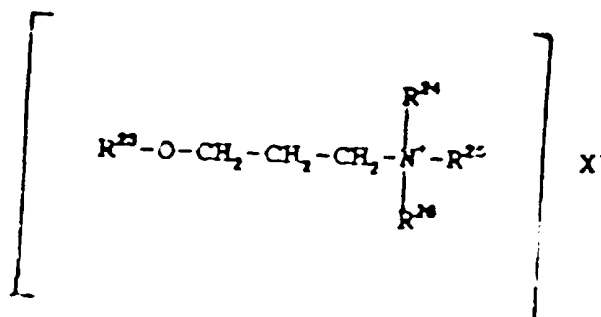
wherein:

R^{13} is selected from the group consisting of $C_{14}-C_{22}$ alkyl and $C_{14}-C_{22}$ alkenyl, wherein the alkyl or alkenyl optionally contains one to three substituents selected from methyl and ethyl;

the remaining R groups are each independently selected from the group consisting of hydrogen, C_1-C_3 straight chain alkyl; and

X^- has the same meaning as described in Formula I;

(e) compounds of Formula V:



Formula V

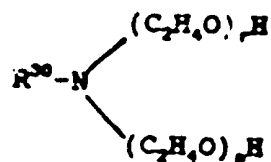
wherein:

R^{23} is selected from the group consisting of C_1-C_{14} alkyl and C_3-C_{14} alkenyl, where the alkyl and alkenyl optionally have one to three substituents selected from methyl and ethyl; and

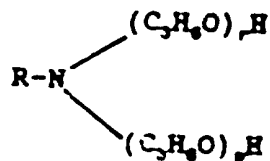
each of R^{24} , R^{25} , and R^{26} are independently selected from the group consisting of C_1-C_4 alkyl, C_3-C_4 alkenyl, $(CH_2-CH_2-O)_nH$ and $(CH_2-CH_2-CH_2-O)_nH$ where n = a number from 1 to 4 inclusive;

and

(D) an alkoxyated amine selected from ethoxylated amines of Formula VI and propoxylated amines of Formula VII:



Formula VI



Formula VII

wherein R^{30} is a member of the group consisting of straight chain alkyls having 8 to 22 carbons, optionally having one to three substituents selected from methyl and ethyl; and r and p each stand for integers such that r and p each must have a value of at least one, are selected independently, and the sum of $r + p$ is a number from two to 12 inclusive.

17. A method as claimed in Claim 16 wherein for any of the R groups listed in Formulae I through V, any carbon atom (a) attached to the nitrogen or phosphorous, (b) adjacent to the nitrogen or phosphorous or (c) next adjacent to the nitrogen, may also be substituted by at least one electron withdrawing groups selected from the group consisting of chlorine, fluorine, CH_2F and CF_3 , provided that chlorine and fluorine are not attached to the nitrogen or phosphorous.
18. The method as claimed in Claim 16 wherein the chelate is selected from the group consisting of ethylenediaminetetracetic acid; sodium tripolyphosphate; ethylenediaminetetracetic acid; diethylenetriaminepentacetic acid; N-(hydroxymethyl)-ethylenediaminetriacetic acid; triethanolamine; diethylenetriaminepenta(methylenephosphonic) acid; and nitrilotriacetic acid.

19. The method as claimed in Claim 16 wherein the alkali is selected from the group consisting of sodium hydroxide, sodium carbonate and calcium hydroxide.
20. The method as claimed in Claim 16 wherein the quaternary ammonium compound is selected from the group consisting of octadecyltrimethylammonium bromide; and cetyltrimethyl-ammonium bromide.
21. A pulp as made by the method of Claim 1.